

PATENT SPECIFICATION



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(Patent of Addition to No. 391,168: dated Sept. 20, 1930.)

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(Under Section 91, Sub-sections (2) and (4) (a) of the Patents and Designs Acts, 1907 to 1932, a single Complete Specification was left in respect of this Application and of Application No. 22089/33 (428,445), and was laid open to inspection on Feb. 12, 1934.)

COMPLETE SPECIFICATION

Improvements in Methods of Preparing Fluorine Derivatives of Hydro-carbons

We, KINETIC CHEMICALS, INC., a corporation organized and existing under the laws of the State of Delaware, United States of America, located at Du Pont Building, Wilmington, States of Delaware, United States of America, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to improvements or modifications of the methods of fluorinating acyclic hydrocarbons, or aryl derivatives thereof, described and claimed in Specification No. 391,168.

In the parent specification referred to, the fluorination is effected in the presence of a catalyst which consists of a halide of a metal whose halide has the property of mutually exchanging its halogen with hydrogen fluoride, and whose fluoride has the property of mutually exchanging halogen with the halogen derivatives of the hydrocarbon whose fluoride it is desired to obtain. Antimony halides, particularly antimony fluoro-chlorides are disclosed as suitable catalysts. The catalyst is desirably maintained in the liquid state.

Liquid catalysts are subject to considerable loss by volatilization necessitating recovery apparatus, while they tend to increase the hazards involved in working the process particularly when they are toxic in character.

According to this invention acyclic hydrocarbons or aryl derivatives thereof are fluorinated by reacting the hydrocarbons containing halogen, other than fluorine, with hydrofluoric acid in the presence of a catalyst formed of or comprising a halide of copper, silver, gold, zinc, cadmium, mercury, vanadium, manganese, iron, cobalt, nickel

or platinum.

The metal halides may be carried on an absorbent solid body, such as carbon or alundum.

A particularly good catalyst is ferric chloride on activated carbon. The metal halide, when it is used in combination with an absorbent material, may be compounded with the absorbent material in any suitable manner,—chemical or physical, including mechanical mixing, as will occur to one skilled in the art.

Metal halides which may be used alone or in combination with one another or with sodium or calcium chlorides or with absorbent material such as activated carbon include AgCl , CuCl_2 , FeCl_3 , VOCl_3 , and MnCl_2 . Examples of suitable combinations are $\text{HgCl}_2 + \text{MnCl}_2 + \text{NaCl} + \text{CuCl}_2$; $\text{MnCl}_2 + \text{AgCl}$; $\text{ZnCl}_2 + \text{CaCl}_2$; and $\text{FeCl}_3 + \text{CuCl}_2 + \text{HgCl}_2$, carried by alundum; FeCl_3 on steel wool; and activated carbon in combination with one or more of the chlorides of the following: Cu, Pt, Hg, V, Ag, Ni, Co, Cd, Zn and Fe. The heavy metal halides are preferred, particularly the chlorides. The metal halide and/or the hydrocarbon halide to be fluorinated may be formed in situ prior to effecting the fluorination.

The original metal halides may be partially or completely changed to one or more other halides in the course of the reaction. Certain halides, e.g. those of gold and platinum, may be reduced to the metal during the reaction, without materially affecting the catalytic efficiency; thus, it has been found that metallic platinum on an inert or active support acts as a fluorinating catalyst.

The formation of the parent hydrocarbon halide in situ may be effected by initially introducing a chlorinating agent, for example, chlorine or antimony pentachloride. In this way acyclic hydro-

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carbons or their aryl derivatives may be used as raw material.

Suitable apparatus for effecting the reaction may consist of vaporizers for vaporizing the hydrogen fluoride and acyclic hydrocarbon halide, a heated reaction chamber containing the catalyst through which the vaporized reagents are simultaneously passed, scrubbers containing alkali for removing excess acid from the reaction vapors, and scrubbers containing strong sulphuric acid or other suitable dehydrating agent for drying the gases, and finally liquefying and storing devices. Traps, gauges, valves and additional inlets etc. may be disposed at convenient places in the system as will readily occur to one skilled in the art. Those portions of the apparatus which come into contact with the hydrogen halide during the reaction are usually made of or lined with some corrosion resistant material. Copper or monel metal are suitable; in addition it has been discovered by us that mild steel, chromium alloy steel and molybdenum alloy steel are also satisfactory and these substances withstand high temperatures and pressures, which may be used, much better than materials such as copper. The hydrogen halide removing scrubbers may however sometimes with advantage be constructed of phenol-formaldehyde resins or of lead. For those parts of the apparatus following the removal of the corroding materials, ordinary construction materials may be used: cast iron, wrought iron, steel etc.

In regard to this we may remark that we are aware of Specification No. 359,997 which discloses the use of sheet steel and Monel metal for the reaction chamber and fractionating column of an apparatus for use in the manufacture of fluorine-containing derivatives of hydrocarbons in which the fluorine for replacing the halogen atoms in an aliphatic hydrocarbon halide is obtained from antimony trifluoride in the presence of antimony pentachloride acting as a catalyst.

In the preferred method of this invention, the metal halide is fixed on a pervious support which is desirably rigid enough to withstand disintegration during the reaction. The combination of a metal halide of the kind referred to, and carbon gives better results at lower temperatures than does the halide per se. Thus copper chloride on alundum (a relatively inert support) does not effectively fluorinate carbon tetrachloride below 400° C. But a combination of copper chloride and activated carbon gives excellent results at 250° C. Similarly ferric chloride and carbon combined effect 70—90% conver-

sion of the hydrogen fluoride at 100—200° C., whereas when used alone at this temperature ferric chloride effects only slight fluorination of carbon tetrachloride.

The carbon may be of any origin; charcoal obtained by destructive distillation of carbonaceous material is suitable. The carbon should preferably be absorptive, while activated and acid washed carbons give particularly good results. It is in general desirable that the physical form of the catalyst be such that it does not tend to form dust and pass out of the catalyst chamber with the gas stream.

While the reaction is preferably effected in the vapor phase, the temperature and pressure may be so adjusted that at least one of the reagents is in liquid phase when in contact with the catalyst. HF is a liquid at 80° C. under a pressure of about 5—6 atmospheres.

The temperature at which the reaction may be effected varies over a wide range, depending upon the material to be fluorinated and the nature of the catalyst. Carbon tetrachloride may be satisfactorily fluorinated at 250°—450° using a metal halide on a substantially inert support such as alundum; trifluorotrichloroethane is similarly fluorinated at about 450—550° C. A catalytically active support lowers the permissible temperature. Thus chloroform and carbon tetrachloride can satisfactorily be fluorinated at 100°—200° C. and trifluorotrichloroethane at 350°—450° C. using activated carbon impregnated with metal halide.

Superatmospheric pressures are advantageously used especially in fluorinating compounds which split off a halogen acid at high temperature; high pressure also allows a greater capacity per unit volume of catalyst.

It will be recognized, that the invention is applicable to the fluorination of a large number of halogen-containing carbon compounds. As specific examples of such compounds may be mentioned methylene chloride (CH_2Cl_2), fluoro-trichloro-methane, (CFCl_3), ethyl chloride ($\text{CH}_3\text{CH}_2\text{Cl}$), ethyl bromide ($\text{CH}_3\text{CH}_2\text{Br}$), isopropyl bromide ($\text{CH}_3\text{CHBrCH}_3$), ethylene dibromide ($\text{CH}_2\text{Br}-\text{CH}_2\text{Br}$), tetrachloro-ethane ($\text{CHCl}_2-\text{CHCl}_2$), trichloro-ethylene ($\text{CHCl}=\text{CCl}_2$), chloroform (CHCl_3), bromoform (CHBr_3), iodoform (CHI_3), carbon tetrachloride (CCl_4), trifluoro-trichloro-ethane ($\text{C}_2\text{F}_3\text{Cl}_3$), symmetrical dichloro-ethane ($\text{CH}_2\text{Cl}-\text{CH}_2\text{Cl}$), hexachloro-ethane (C_2Cl_6), difluoro-tetrachloro-ethane ($\text{C}_2\text{Cl}_4\text{F}_2$), tetrachloro-ethylene ($\text{Cl}_2\text{C}=\text{CCl}_2$) and halogen derivatives of higher members of the aliphatic series. As further examples of compounds containing an acyclic carbon atom having attached

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thereto a halogen other than fluorine may be mentioned benzo - trichloride ($C_6H_5CCl_3$), benzo - difluoro - chloride ($C_6H_5CF_2Cl$), benzo - fluoro - dichloride ($C_6H_5CFCl_2$) and ring-substituted benzo-trichlorides containing substituents such as, for example, alkyl groups (methyl, ethyl, propyl, etc.) and halogens (e.g. chlorine and bromine). In fluorinating benzo-trichloride derivatives containing chlorine atoms in the aryl portion thereof, it has been noted that the chlorine atoms in the acyclic portion may be replaced by fluorine without affecting the chlorine atoms in the aryl portion.

Where the original acyclic halogen derivative contains hydrogen, a substitution of halogen for hydrogen may occur during the fluorination operation if a free halogen such as chlorine is present during the fluorination reaction. Examples of such reactions are those taking place when methylene chloride or tetrachloro-ethane are fluorinated.

When the original acyclic halogen derivative is unsaturated, the addition of halogen and the introduction of fluorine may take place in the same operation. For instance, fluoro-chloro derivatives of ethane may be prepared by passing tetrachloro-ethylene or trichloro-ethylene, hydrogen fluoride and chlorine through the catalyst under suitable conditions of temperature and pressure.

The hydrogen fluoride may contain impurities such as water.

In the following Examples the parts are by weight.

EXAMPLE 1.

Gaseous hydrogen fluoride and carbon tetrachloride in proportions corresponding to about 20 parts of hydrogen fluoride and 300 parts carbon tetrachloride were hourly passed through 300 parts of a mixture of 90% charcoal and 10% cuprous chloride disposed in a chromium alloy steel tube having a length approximately 10 times its diameter. The catalyst was maintained at a temperature of 250° C. by means of external electrical heating coils.

The gases after passage through the catalyst consisted chiefly of hydrogen chloride, difluoro - dichloro - methane, fluoro - trichloro - methane, hydrogen fluoride and carbon tetrachloride. The hydrogen chloride and hydrogen fluoride were largely removed by treatment with water. The gas stream was further purified by scrubbing through an aqueous 9-10% caustic solution and then through a 90-95% sulphuric acid solution. During the operation, the caustic and sulphuric acid scrubbers and the intermediate trap were held at a temperature of about 50° to 60° C. The product, condensed at

a temperature of about -40° to -50° C. and recovered in liquid form, was then fractionally distilled to separate difluoro-dichloro-methane, fluoro-trichloro-methane and carbon tetrachloride. The overall-yield of fluorinated derivatives, based on hydrogen fluoride was about 82%.

EXAMPLE 2.

The vapors of 20 parts of substantially anhydrous hydrogen fluoride and 310 parts of carbon tetrachloride were hourly passed through 300 parts of a catalyst composed of charcoal and ferric chloride in an iron reactor similar in design to that described in Example 8. The temperature of the catalyst was maintained at about 145-155° C. This catalyst was prepared by mixing one part of sublimed ferric chloride with ten parts of charcoal.

The mixture of gases leaving the catalyst consisted of hydrogen chloride, difluoro-dichloro-methane, fluoro-dichloro-methane and unreacted hydrogen fluoride and carbon tetrachloride. The gas mixture was passed through water which removed the greater part of the hydrogen halides. The gases were then further purified by washing with caustic soda solution and then drying with sulphuric acid (specific gravity 1.80). During five hours of continuous operation a yield of 88% of fluorine derivatives, based upon hydrogen fluoride, was obtained.

EXAMPLE 3.

There were hourly added 120 parts of difluoro-dichloro-methane and 20 parts of hydrogen fluoride to 300 parts of a catalyst, consisting of 90% activated carbon and 10% cuprous chloride, and maintained within the temperature range 350°-450° C.

The exit gases consisted of a mixture of trifluoro - chloro - methane, difluoro - dichloro-methane, hydrogen chloride and hydrogen fluoride. The fluoro-chloro derivatives were purified by passing successively through water, aqueous sodium hydroxide solution and sulphuric acid (specific gravity 1.80) all of which were held at 20-30° C. The purified gases were, with the exception of a small amount of tri-fluoro-chloro-methane, liquefied by means of a condenser, maintained at about -75° C.

The uncondensed material was collected in a gasometer. The liquid was subjected to suitable fractional distillation, whereupon it yielded trifluoro-chloro-methane (boiling point about -80° C.) and difluoro-dichloro-methane.

The yield of trifluoro-chloro-methane, based upon hydrogen fluoride, was 50-55%; the yield based upon consumed difluoro-dichloro-methane was essentially quantitative.

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EXAMPLE 4.

To 300 parts of a catalyst consisting of 90% activated carbon and 10% cuprous chloride, maintained at 300°-400° C., there were hourly added at a uniform rate 100 parts of carbon tetrachloride and 50 parts of hydrogen fluoride. The exit gases were purified and condensed in the same manner as in Example 10.

The liquefied product consisted primarily of a mixture of trifluoro-chloro-methane and difluoro-dichloro-methane. Some fluoro-trichloro-methane was also recovered. The combined yield of fluoro derivatives, based on carbon tetrachloride, was above 90%; the yield, based on hydrogen fluoride, was above 70%.

EXAMPLE 5.

Substantially anhydrous hydrogen fluoride was allowed to vaporize and the vapors passed through trifluoro-trichloro-ethane heated to a temperature of about 42° C. The mixture of vapors was then passed through a column of pieces of alundum, impregnated with vanadium tetrachloride. The catalyst was contained in a tube constructed of a molybdenum-containing steel, and was maintained at a temperature of about 500° C. Hydrogen chloride, tetrafluoro-dichloro-ethane and penta-fluoro-chloro-ethane were produced.

The gas mixture was scrubbed with water and an aqueous alkali metal hydroxide solution and dried with sulphuric acid. On condensing the product in an alcohol-carbon dioxide ice bath, a liquid which boiled at about 0° C. was obtained. This liquid was a mixture of penta-fluoro-chloro-ethane, tetra-fluoro-dichloro-ethane and unconverted trifluoro-trichloro-ethane. Under the conditions of reaction approximately 50% of the hydrogen fluoride was utilized. The liquid mixture above described was subject to fractional distillation and the penta-fluoro-chloro-ethane (C_2F_5Cl) and tetra-fluoro-dichloro-ethane ($C_2F_4Cl_2$) were isolated. Penta-fluoro-chloro-ethane which is apparently a new product and one not previously isolated boils at about -40° C. under atmospheric pressure. Tetra-fluoro-dichloro-ethane boils at about +4° C. under atmospheric pressure.

EXAMPLE 6.

Hydrogen fluoride was allowed to boil gently and the vapors passed through fluoro-trichloro-methane held at a temperature of about 20-25° C. The gaseous mixture of the two compounds was then passed through 400 parts of a heated column of alundum fragments impregnated with manganese chloride. The temperature of the catalyst was maintained at about 400° C. The rate of feed

of hydrogen chloride averaged about 20 parts per hour. The gases leaving the catalyst were washed consecutively with water, caustic and sulphuric acid. The remaining gases when condensed at a temperature of about -50° C. produced a colorless liquid which began to boil at about -25° C. This product was a mixture consisting largely of difluoro-dichloro-methane and fluoro-trichloro-methane. These two components were obtained in a pure state by fractional distillation of the above described mixture, the distillation preferably being carried out under superatmospheric pressure. The yield of difluoro-dichloro-methane, based upon hydrogen fluoride, was about 74%.

The products of the invention find application for various commercial purposes. Thus, difluoro-dichloro-methane tetrafluoro-dichloro-ethane, fluoro-dichloro-methane ($CHFCl_2$) and fluoro-trichloro-methane (CCl_3F) are widely used as refrigerants. The new product penta-fluoro-chloro-ethane, described in Example 5 also possesses very desirable properties for low temperature refrigeration. Some of the higher boiling compounds, such as trifluoro-trichloro-ethane and fluoro-trichloro-methane, are generally applicable for use as solvents or reaction media. Moreover, many of the products investigated have been found to be advantageous in that they are odorless, non-inflammable, non-corrosive and non-toxic.

We are aware that it has previously been proposed to manufacture methane derivatives containing chlorine and fluorine by acting with hydrogen fluoride upon carbon tetrachloride vapour in the presence of a mixture of antimony trichloride and antimony pentachloride which might be carried on a porous substances, such as coke.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed we declare that what we claim is:—

1. An improved method of fluorinating acyclic hydrocarbons or aryl derivatives thereof by reacting a hydrocarbon halide containing halogen, other than fluorine, and hydrofluoric acid in the presence of a catalyst formed of or comprising a halide of copper, silver, gold, zinc, cadmium, mercury, vanadium, manganese, iron, cobalt, nickel or platinum.

2. An improved method as claimed in Claim 1 wherein the catalyst body is formed of or comprises a mixture of a plurality of the metal halides.

3. An improved method, as claimed in Claim 1, in which the metal halide is

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carried on a solid support.

4. An improved method as claimed in Claim 3, in which the solid support or body consists of or comprises carbon, preferably activated.

5. An improved method as claimed in Claim 3, in which the solid support or body comprises alundum.

6. An improved method as claimed in any one or more of the preceding claims in which the metal halide, and/or hydrocarbon halide containing halogen other than fluorine, is formed in situ in the reaction mixture prior to effecting the fluorination.

7. An improved method, as claimed in any one or more of the preceding claims, in which a heavy metal halide is used.

8. An improved method as claimed in

Claim 7 in which the catalytic element consists of activated carbon impregnated with iron or copper chloride.

9. An improved method as claimed in any one or more of the preceding claims, which comprises effecting the reaction in apparatus constructed wholly or in part of mild steel, chromium alloy steel, or molybdenum alloy steel.

10. The methods of fluorinating acyclic hydrocarbons substantially as set forth in the foregoing Examples.

11. The improved methods of fluorinating acyclic hydrocarbons or aryl derivatives thereof, substantially as hereinbefore described.

Dated this 5th day of August, 1933.
MARKS & CLERK.

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